

WHAT IS CLAIMED:

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1. A combinatorial library comprising
a plurality of at least six different complexes, each formed of at
least one complexing agent and at least two non-biopolymer ligands that are reversibly
bonded to the complexing agent, wherein each different complex in said library has
different ligands bonded to the complexing agent.
2. A combinatorial library according to claim 1, wherein each of said
plurality of complexes has the formula $Z(A^i)_n$, wherein Z is a complexing agent capable
of reversibly binding to two or more ligands, each A^i is a non-biopolymer ligand capable
of reversibly binding to Z and is independently selected from a group of non-biopolymer
ligands having at least three different members, n is the number of A's that are reversibly
bonded to Z and is an integer equal to two or greater, and i is an index number for each A
and is an integer from 1 to n.
3. A combinatorial library according to claim 2, wherein each of said
plurality of complexes has the formula $Z(A^1)(A^2)(A^i)_{n-2}$, wherein A^1 and A^2 are non-
biopolymer ligands capable of reversibly binding to Z and are independently selected
from a group of non-biopolymer ligands having at least three different members and i is
an index number for each A and is an integer from 3 to n.
4. A combinatorial library according to claim 3, wherein said
combinatorial library comprises complexes having the formulae $Z(B1)(B1)(A^i)_{n-2}$,
 $Z(B1)(B2)(A^i)_{n-2}$, $Z(B1)(B3)(A^i)_{n-2}$, $Z(B2)(B2)(A^i)_{n-2}$, $Z(B2)(B3)(A^i)_{n-2}$, and
 $Z(B3)(B3)(A^i)_{n-2}$; B1, B2, and B3 are different non-biopolymer ligands and are members
of the group from which each A^i is selected; and i is an index number for each A and is an
integer from 3 to n.
5. A combinatorial library according to claim 2, wherein each of said
plurality of complexes has the formula $Z(A^1)(A^i)_{n-1}$, wherein A^1 is a non-biopolymer
ligand capable of reversibly binding to Z and is independently selected from a group of
non-biopolymer ligands having at least three different members; i is an index number for

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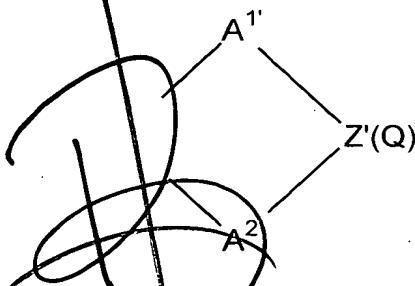
each A and is an integer from 3 to n; and Z, A¹, and each Aⁱ are selected so that the reactions $Z(A^i)_{n-1} + A^1 \rightarrow Z(A^1)(A^i)_{n-1}$ and $Z(A^1)(A^i)_{n-1} \rightarrow Z(A^i)_{n-1} + A^1$ each have a rate constant of greater than about 2 per second.

- 5 6. A combinatorial library according to claim 2, wherein at least one of Aⁱ is a DNA intercalator or a major or minor groove DNA binder.

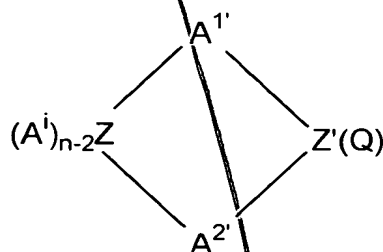
~~7 A combinatorial library according to claim 2, wherein Z is a transition metal.~~

- 10 8. A combinatorial library according to claim 2, wherein at least one Aⁱ has the formula -A'Z'(Q), Z' is a second complexing agent identical to or different than Z, A' is a pluridentate non-biopolymer ligand, and Q is one or more non-biopolymer ligands .

- 15 9. A combinatorial library according to claim 3, wherein A¹ and A², taken together, have the formula:



20 where A'¹ and A'² are pluridentate non-biopolymer ligands, Z' is a second complexing agent identical to or different than Z, and Q is one or more non-biopolymer ligands so that Z(A¹)(A²)(Aⁱ)_{n-2} has the formula:



10. A combinatorial library according to claim 1, wherein said combinatorial library comprises a plurality of at least 100 different complexes.

5 11. A composition comprising:
a combinatorial library according to claim 1, and
a receptor in contact with the combinatorial library, wherein some of the complexes bind preferentially to said receptor.

10 12. A composition according to claim 11, wherein said receptor is a biological receptor.

13. A composition according to claim 11, wherein said receptor is an immobilized receptor.

15 14. A composition according to claim 11, wherein each of the plurality of complexes has the formula $Z(A^i)_n$, wherein Z is a complexing agent capable of reversibly binding to two or more ligands, each A^i is a non-biopolymer ligand capable of reversibly binding to Z and is independently selected from a group of non-biopolymer ligands having at least three different members, n is the number of A's that are reversibly bonded to Z and is an integer equal to two or greater, and i is an index number for each A and is an integer from 1 to n.

25 15. A composition according to claim 14, wherein each of the plurality of complexes has the formula $Z(A^1)(A^2)(A^i)_{n-2}$, wherein A^1 and A^2 are non-biopolymer ligands capable of reversibly binding to Z and are independently selected from a group of non-biopolymer ligands having at least three different members and i is an index number for each A and is an integer from 3 to n.

30 16. A composition according to claim 15, wherein said combinatorial library comprises complexes having the formulae $Z(B1)(B1)(A^i)_{n-2}$, $Z(B1)(B2)(A^i)_{n-2}$, $Z(B1)(B3)(A^i)_{n-2}$, $Z(B2)(B2)(A^i)_{n-2}$, $Z(B2)(B3)(A^i)_{n-2}$, and $Z(B3)(B3)(A^i)_{n-2}$; B1, B2, and B3 are different non-biopolymer ligands and are members of the group from which each A^i is selected; and i is an index number for each A and is an integer from 3 to n.

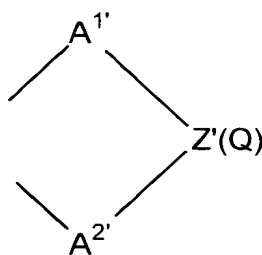
17. A composition according to claim 14, wherein each of the plurality of complexes has the formula $Z(A^1)(A^i)_{n-1}$, wherein A^1 is a non-biopolymer ligand capable of reversibly binding to Z and is independently selected from a group of non-biopolymer ligands having at least three different members; i is an index number for each A and is an integer from 3 to n; and Z, A^1 , and each A^i are selected so that the reactions $Z(A^i)_{n-1} + A^1 \rightarrow Z(A^1)(A^i)_{n-1}$ and $Z(A^1)(A^i)_{n-1} \rightarrow Z(A^i)_{n-1} + A^1$ each have a rate constant of greater than about 2 per second.

18. A composition according to claim 14, wherein at least one of the A^i is a DNA intercalator or a major or minor groove DNA binder.

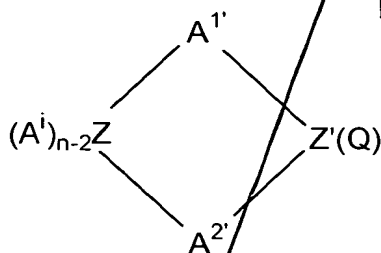
19. A composition according to claim 14, wherein Z is a transition metal.

20. A composition according to claim 14, wherein at least one A^i has the formula $-A'Z'(Q)$, Z' is a second complexing agent identical to or different than Z, A' is a pluridentate non-biopolymer ligand, and Q is one or more non-biopolymer ligands.

21. A composition according to claim 15, wherein A^1 and A^2 , taken together, have the formula:



where $A^{1'}$ and $A^{2'}$ are pluridentate non-biopolymer ligands, Z' is a second complexing agent identical to or different than Z, and Q is one or more non-biopolymer ligands so that $Z(A^1)(A^2)(A^i)_{n-2}$ has the formula:



22. A composition according to claim 12, wherein said combinatorial library comprises a plurality of at least 100 different complexes.

23. A method of identifying a combination of non-biopolymer ligands which bind preferentially to a receptor comprising:
 providing a combinatorial library according to claim 1;
 contacting the combinatorial library with a receptor under conditions effective to preferentially bind a fraction of the plurality of complexes; and
 identifying the fraction of the plurality of complexes which are bound preferentially to the receptor.

24. A method according to claim 23, wherein the receptor is a biological receptor.

25. A method according to claim 23, wherein the receptor is an immobilized receptor.

26. A method according to claim 23, wherein each of the plurality of complexes has the formula $Z(A^i)_n$, wherein Z is a complexing agent capable of reversibly binding to two or more ligands, each A^i is a non-biopolymer ligand capable of reversibly binding to Z and is independently selected from a group of non-biopolymer ligands having at least three different members, n is the number of A's that are reversibly bonded to Z and is an integer equal to two or greater, and i is an index number for each A and is an integer from 1 to n.

27. A method according to claim 26, wherein each of said plurality of complexes has the formula $Z(A^1)(A^2)(A^i)_{n-2}$, wherein A^1 and A^2 are non-biopolymer ligands capable of reversibly binding to Z and are independently selected from a group of non-biopolymer ligands having at least three different members and i is an index number for each A and is an integer from 3 to n.

28. A method according to claim 27, wherein said combinatorial library comprises complexes having the formulae $Z(B1)(B1)(A^i)_{n-2}$, $Z(B1)(B2)(A^i)_{n-2}$, $Z(B1)(B3)(A^i)_{n-2}$, $Z(B2)(B2)(A^i)_{n-2}$, $Z(B2)(B3)(A^i)_{n-2}$, and $Z(B3)(B3)(A^i)_{n-2}$; B1, B2, and B3 are different non-biopolymer ligands and are members of the group from which each A^i is selected; and i is an index number for each A and is an integer from 3 to n.

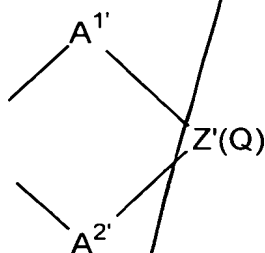
29. A method according to claim 26, wherein each of said plurality of complexes has the formula $Z(A^1)(A^i)_{n-1}$, wherein A^1 is a non-biopolymer ligand capable of reversibly binding to Z and is independently selected from a group of non-biopolymer ligands having at least three different members; i is an index number for each A and is an integer from 3 to n; and Z, A^1 , and each A^i are selected so that the reactions $Z(A^i)_{n-1} + A^1 \rightarrow Z(A^1)(A^i)_{n-1}$ and $Z(A^1)(A^i)_{n-1} \rightarrow Z(A^i)_{n-1} + A^1$ each have a rate constant of greater than about 2 per second.

30. A method according to claim 26, wherein at least one A^i is a DNA intercalator or a major or minor groove DNA binder.

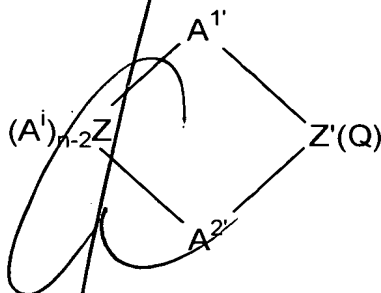
31. A method according to claim 26, wherein Z is a transition metal.

32. A method according to claim 26, wherein at least one A^i has the formula $-A'Z'(Q)$, Z' is a second complexing agent identical to or different than Z, A' is a pluridentate non-biopolymer ligand, and Q is one or more non-biopolymer ligands.

33. A method according to claim 27, wherein A^1 and A^2 , taken together, have the formula:



where $A^{1'}$ and $A^{2'}$ are pluridentate non-biopolymer ligands, Z' is a second complexing agent identical to or different than Z , and Q is one or more non-biopolymer ligands so that $Z(A^1)(A^2)(A^i)_{n-2}$ has the formula:



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34. A method according to claim 23, wherein the combinatorial library comprises a plurality of at least 100 different complexes.

10 35. A method according to claim 26, wherein some of $Z(A^i)_n$ bind more strongly than others of $Z(A^i)_n$ to the receptor.

36. A method according to claim 23, wherein said providing a combinatorial library comprises:

15 contacting a compound containing a complexing agent with a plurality of at least three different non-biopolymer ligands.

37. A method according to claim 26, wherein said providing a combinatorial library comprises:

20 contacting one part of a complexing agent, Z , or a salt thereof with m^1 parts of A^1 and m^i parts of A^i , wherein A^1 and each A^i are non-biopolymer ligands, i is an integer from 2 to k , k is an integer equal to or greater than 3 and represents the number

of members in the group of at least three different non-biopolymer ligands from which the at least two non-biopolymer ligands are selected, and the sum of m^i and Σm^i from $i=2$ to k equals n under conditions effective to form a substantially statistical mixture of $Z(A^i)_n$.

5 38. A method according to claim 26, wherein said providing a
combinatorial library comprises:

contacting a complex, $Z(A^1)_n$, with two or more complexes $Z(A^i)_n$, wherein A^1 and each A^i are non-biopolymer ligands, i is an integer from 2 to k , and k is an integer equal to or greater than 3 and represents the number of members in the group of at least three different non-biopolymer ligands from which the at least two non-biopolymer ligands are selected.

39. A method of producing a combinatorial library according to claim 2 comprising:

contacting one part of a complexing agent, Z, or a salt thereof with
m¹ parts of A¹ and mⁱ parts of Aⁱ under conditions effective to form a substantially
statistical mixture of Z(Aⁱ)_n, wherein A¹ and each Aⁱ are non-biopolymer ligands, i is an
integer from 2 to k, k is an integer equal to or greater than 3 and represents the number of
members in the group of at least three different non-biopolymer ligands from which the at
least two non-biopolymer ligands are selected, and the sum of m¹ and Σ mⁱ from i=2 to k
equals n.

40. A method of producing a combinatorial library according to claim 2 comprising:

contacting a complex, $Z(A^1)_n$, with two or more complexes $Z(A^i)_n$
under conditions effective to form a substantially statistical mixture of $Z(A^i)_n$, wherein A^1
and each A^i are non-biopolymer ligands, i is an integer from 2 to k , and k is an integer
equal to or greater than 3 and represents the number of members in the group of at least
three different non-biopolymer ligands from which the at least two non-biopolymer
ligands are selected.

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